Chemical Kinetics of Intermediates in the Autoxidation of SO_2

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The autoxidation of aqueous solutions of sulfur dioxide (sulfite, bisulfite) is a classic problem in chemistry. Basic features of this reaction have been known since early in this century, when it was established that the reaction is trace metal ion catalyzed (1) and most likely involved free radicals (2). Certain chemical effects associated with sulfite autoxidation were noted also. Before the turn of the century, it was reported that sulfite would induce the oxidation of transition metal ions (3) and it was reported later that the oxidation of organic compounds was brought about during sulfite autoxidation (4). Conversly, it was reported also that organic compounds could serve as inhibitors of sulfite autoxidation (5).

Over the past century there have been a great many studies on sulfite autoxidation (6), including studies on the rate of the reaction in the presence of catalysts and inhibitors, measurements of the amounts of sulfite and dithionate found under various conditions, the determination of the products arising from the addition of organic (including biochemical) compounds, and studies on the effects of mixed catalysts. Yet, a quantitative understanding of the reaction has been elusive (7,8). This is due largely to a lack of quantitative data on the elementary steps in the overall reaction, including data on the rates of the free radical reactions likely to be important.

Recently, we have carried out studies on the free radical chemistry of sulfite. These studies have included kinetic measurements on the reactions of organic and inorganic free radicals with sulfite and bisulfite, and on the reactions of the sulfite derived radicals SO_3^- and SO_5^- with organic and inorganic substrates. In this paper, I will review some of our results and results from other laboratories on the radical chemistry of sulfite and discuss these results in relation to the problem of SO_2 autoxidation.

Rate constants for the radical reactions were carried out using pulse radiolysis. Briefly, a N_2O saturated solution is pulse irradiated, with high energy electrons, producing OH radicals.

$$H_2O \qquad OH,\ H,\ e^-_{aq}$$

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + OH + OH^-$$

(The small amount of H atoms produced usually does not interfere.) The OH reacts with sulfite or bisulfite to produce the $\dot{S}O_3^-$ radical

$$OH + HSO_3^- \rightarrow H_2O + \dot{S}O_3^-$$

$$OH + SO_3^{2-} \rightarrow OH^- + \dot{S}O_3^-$$

or with some other organic or inorganic substrate to produce another desired radical

$$\mathrm{OH} + \mathrm{S} \rightarrow \mathrm{OH}^- + \dot{\mathrm{S}}^+$$

The optical absorption of $\dot{S}O_3^-$ exhibits $\lambda_{max} = 225$ nm with $\varepsilon_{max} = 1000 M^{-1} cm^{-1}$ (9). This absorption is not convenient for following the reactions of $\dot{S}O_3^-$ with other substrates since the uv absorption of most other substrates or their radicals mask this relatively weak absorption. Therefore, the optical absorption of the other radical product (or reactant) was monitored. For example, in the reaction of $\dot{S}O_3^-$ with ascorbate, the ascorbate radical absorption at 360 nm was monitored; the reaction of the radical I_2^- with HSO_3^-/SO_3^{2-} was monitored at 380 nm, the absorption maxima for I_2^-.

Oxidation of sulfite and bisulfite by free radicals

We have found that sulfite and bisulfite undergo one-electron oxidation by many free radicals to produce $\dot{S}O_3^-$. Rate constants determined for selected radicals are given in Table 1. Measurement of the rate constant over a wide range of pH has, in some cases, allowed the separate determination of rate constants for the oxidation of sulfite and bisulfite. The very strong oxidants OH and SO_4^- react very rapidly and oxidize bisulfite faster than sulfite. For radicals are weaker oxidants, the reaction with sulfite is the faster. For example, with Br_2^- the ratio of rate constants for sulfite to bisulfite is about 4; for the even weaker oxidant I_2^- the ratio is about 200. For the dimethylaniline radical cation, the reaction with sulfite is very fast ($k \sim 10^9 M^{-1} s^{-1}$) while the reaction with bisulfite is too slow to measure ($k < 8 \times 10^5 M^{-1} s^{-1}$).

These observations on both the relative and absolute rates of reaction of radicals with sulfite and bisulfite can be compared with observations made on the reactions of transition metal ions with SO_2 solutions. Typically, a strong, positive pH dependence is measured for these reactions. This usually is interpreted as suggesting that sulfite, not bisulfite, is the important reactant. Since these metal ions are relatively weak oxidants ($E < 1V$), this conclusion would appear to be justified. For Mn(III), which is a strong oxidant ($E_o \sim 1.4V$), reaction with bisulfite appeared to be important (10).

Reactions of sulfite radicals

Rate constants for the reactions of $\dot{S}O_3^-$ with a wide variety of organic compounds have been measured; some of these results are summarized in Table 2. The sulfite radical was found to oxidize ascorbate, trolox (a water soluble tocopherol derivative), methoxyphenol, hydroquinone and other phenolic compounds, sulfonated hydroquinones, phenylenediamines, and phenothiazines with rate constants ranging to $10^9 M^{-1} s^{-1}$.

Rate constants for one-electron redox reactions depend upon the relative reduction potentials of the reactants. We have been able to derive the one-electron reduction potential of $\dot{S}O_3^-$ by measuring the equilibrium constant for its reaction with chlorpromazine

$$SO_3^- + ClPz \rightleftarrows SO_3^{2-} + ClPz^+$$

This led to a reduction potential of 0.84V v. NHE at pH 3.6 for the couple SO_3^-/HSO_3^-. The reduction potential of the SO_3^-/SO_3^{2-} couple in basic solution is calculated (from the pKa of $HSO_3^- \rightleftarrows H^+ + SO_3^{2-}$) to be 0.63V. This change in potential helps explain why SO_3^{2-} is oxidized by the same oxidant more readily than HSO_3^-.

Using the reduction potential for SO_3^- we can calculate the one-electron reduction potential for SO_4^{2-}. In basic solution, this can be done by subtracting $E(SO_3^-)=0.63V$ from twice the two-electron reduction potential for sulfite

$$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-, \; E = -0.92V.$$

This leads to

$$SO_4^{2-} + H_2O + e^- \rightarrow SO_3^- + 2OH^-, \; E= -2.47V.$$

Although this suggests that $\dot{S}O_3^-$ can act as a strong reductant, this calculation possibly seriously overstates its actual reducing power. This is because the initial product of the electron transfer would be SO_3, not SO_4^{2-} which results from subsequent hydrolysis. The enthalpy difference between $SO_3 \cdot_{aq}$ and SO_4^{2-} is not known, but probably is greater than that between $SO_2 \cdot_{aq}$ and SO_3^{2-} (3.24V) (11). If this is correct, the one electron potential for the SO_3/SO_3^- couple would be greater than 0.77 V and $\dot{S}O_3^-$ would therefore be a very poor reductant.

Possibly the most important reaction of the sulfite radical in autoxidation systems is with molecular oxygen. The reaction has been suggested to lead either to O_2^- or to the peroxy radical $S\dot{O}_5^-$

$$\dot{S}O_3^- + O_2 \rightarrow SO_3 + O_2^-$$

$$\dot{S}O_3^- + O_2 \rightarrow S\dot{O}_5^- \quad .$$

By determining the reactivity of the product radical with ascorbate, we were able to demonstrate that the former reaction is very unlikely and concluded that the product is the peroxy radical, $S\dot{O}_5^-$.

Reactions of the peroxysulfate radical

In Table 3 are listed some rate constants for reactions of $S\dot{O}_5^-$, along with some values for $\dot{S}O_3^-$ and $\dot{S}O_4^-$ for comparison. The results show that $S\dot{O}_5^-$ is a stronger oxidant than $\dot{S}O_3^-$ (but weaker than $\dot{S}O_4^-$) and we have estimated its one-electron reduction potential to be about 1.1V at pH

7. Of particular interest is the ability of $S\dot{O}_5^-$ to oxidize certain substances (aniline and dimethylaniline, for example) which form radicals which are capable of oxidizing sulfite. This can lead to the enhancement of the autoxidation of sulfite through the chain

$$SO_3^- + O_2 \rightarrow SO_5^-$$

$$SO_5^- + X \rightarrow SO_5^{2-} + X^+$$

$$X^+ + SO_3^{2-} \rightarrow X + SO_3^- \; .$$

In sulfite autoxidation, an exceedingly important reaction is that of SO_5^- with SO_3^{2-}/HSO_3^-. We have been able to derive a rate constant for this reaction, but have not been able to establish its mechanism.

Three paths are possible for this reaction

$$\begin{aligned} SO_5^- + SO_3^{2-} + H^+ &\rightarrow HSO_5^- + SO_3^- \\ &\rightarrow SO_4^- + SO_4^{2-} + H^+ \\ &\xrightarrow{H_2O} 2SO_4^- + OH + 2H^+ \end{aligned}$$

Since both OH and SO_4^- very rapidly oxidize SO_3^{2-} to SO_3^-, these paths are indistinguishable in our experiments. The identity of the correct path is quite important since the production of HSO_5^- can lead to possible chain branching steps. We do know that SO_5^- undergoes this one-electron reduction by a host of organic compounds. Further, the rate constants for these reactions are consistant with that derived for the reaction of $S\dot{O}_5^-$ with SO_3^{2-}. I therefore conclude that the mechanism producing HSO_5^- is the most likely.

This product of the one-electron reduction of $S\dot{O}_5^-$ (HSO_5^-, peroxymonosulfate, Caro's acid), is a strong oxidant with a standard two-electron reduction potential of 1.82V (12). A product with the properties of peroxymonosulfate has been observed with a yield up to 30% upon bubbling oxygen through a solution of sodium sulfite (13). This compound can undergo many possible subsequent reactions. From the present point of view, the most important would be the further production of free radicals, most likely upon reaction with transition metal ions, for example

$$\begin{aligned} Fe^{2+} + HSO_5^- &\rightarrow Fe^{3+} + OH + SO_4^{2-} \\ &\rightarrow Fe^{3+} + OH^- + SO_4^- \end{aligned}$$

In a mechanism for the iron catalyzed autoxidation of sulfite, this would be a chain branching step. We have some evidence that the reaction of Fe^{2+} with HSO_5^-, in acid, does lead to free radicals, but is somewhat more complex than written above (14).

Conclusions

It has been apparent for some time that the inhibition of sulfite autoxidation by organic compounds is due to reaction of free radical intermediate with these compounds. Further, it seems likely that the chemical effects associated with SO_2 autoxidation are due to these or other reactive intermediates. Now that the reactivities of many of these intermediates are known, the mechanism of these effects can be begun to be understood. For many organic compounds, like hydroquinone and other phenolic species, reaction with SO_3^- and SO_5^- is possible. Indeed, they prove to be the most efficient inhibitors of SO_2 autoxidation. For other organic compounds like mannitol or fumarate, only reactions with SO_4^- or OH are likely. In some cases, inhibition by direct reaction with HSO_5^- might be possible.

The results we have obtained on the one-electron oxidation of sulftie and bisulfite by free radicals also are important in understanding possible chain initiation and chain carrying steps in SO_2 autoxidation. This is particularly true in systems which do not consist simply of SO_2 and a catalyst. For example, the production and subsequent reaction of halide free radicals could be important in any system containing halogen ions. The observation that many organic free radicals can react with sulfite also could be important in understanding these complex systems. Some organic free radicals can be formed easily by reaction of the parent with O_2. If these radicals react with sulfite but are otherwise stable, they could provide new, efficient, catalysts for SO_2 autoxidation.

Although the study of SO_2 autoxidation is over 100 years old, the direct study of the reactive intermediates is just beginning. In real-world systems, ranging from atmospheric droplets to flue-gas scrubbers, these reactions will take place under a wide range of pH, temperature, and ionic strength. As these reactions become better understood, they can be used to model these sytems and, ultimately to control them.

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Table 1 . Rate Constants for Reactions of Sulfite with Radicals

Reaction	pH	$k(M^{-1}s^{-1})$	reference
$OH + HSO_3^-$	-	$9.5\text{x}10^{9}$	a
$OH + SO_3^{2-}$	-	$5.5\text{x}10^{9}$	a
$SO_4^- + HSO_3^-$	-	$\geq 1\text{x}10^{9}$	b
$SO_4^- + SO_3^{2-}$	-	$\geq 5\text{x}10^{8}$	b
$Cl_2^- + SO_3^{2-}/HSO_3^-$	7	$3.3\text{x}10^{7}$	c
$Br_2^- + HSO_3^-$	4.2	$6.9\text{x}10^{7}$	d
$Br_2^- + SO_3^{2-}$	10	$2.6\text{x}10^{8}$	d
$I_2^- + HSO_3^-$	3	$1.1\text{x}10^{6}$	d
$I_2^- + HSO_3^-/SO_3^{2-}$	6.7	$1\text{x}10^{7}$	d
$I_2^- + SO_3^{2-}$	11	$1.9\text{x}10^{8}$	d
$NH_2 + SO_3^{2-}$	11	NR	d
$C_6H_5O + SO_3^{2}$	11	$1\text{x}10^{7}$	d
$C_6H_5NH_2^+ + HSO_3^-$	2.5	$4.8\text{x}10^{6}$	d
$C_6H_5NH_2^+ + SO_3^{2-}$	*	$4\text{x}10^{9}$	d
$C_6H_5NH + SO_3^{2-}$	13	$<3\text{x}10^{4}$	d
$C_6H_5N(CH_3)_2^+ + HSO_3^-$	3.6	$<8\text{x}10^{5}$	d
$C_6H_5N(CH_3)_2^+ + SO_3^{2-}$	10.9	$9.9\text{x}10^{8}$	d
(chlorpromazine)$^{\cdot +}$ $+HSO_3^-$	3.6	$\sim 5\text{x}10^{5}$	e

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NR No reaction detected ($k<10^5M^{-1}s^{-1}$). The redox potentials for NH_2 and SO_3^- radicals appear to be very similar, judging from rate constants for their reactions with several reactants.

* Calculated from the pH dependence of the rate constant.

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Table 2. Rate constants for Reactions of SO_3^- Radicals with Various Reactants

Reactant	pH	$k(M^{-1}s^{-1})$	reference
ascorbic acid	<3	$<10^{6}$	a
ascorbate ion	5-10	9×10^{6}	a
ascorbate dianion	>12	3×10^{8}	a
trolox	9	$\sim 10^{6}$	a
phenol	11.1	6×10^{5}	b
p-methoxyphenol	9.2	4×10^{7}	b
p-methoxyphenol	12.4	1.2×10^{8}	b
hydroquinone	8.9	4.5×10^{6}	c
hydroquinone	10.5	5.4×10^{7}	c
hydroquinone	12.9	3.2×10^{8}	c
p-phenylenediamine	3.4	$<5 \times 10^{5}$	d
p-phenylenediamine	5.3	4.2×10^{6}	d
p-phenylenediamine	9.3	5.0×10^{7}	d
N,N,N',N'-tetramethyl-p-phenylenediamine	4.5	8.2×10^{6}	d
N,N,N',N'-tetramethyl-p-phenylenediamine	9.5	5.2×10^{8}	d
chlorpromazine	3.6	$\sim 5 \times 10^{6}$	b
O_2	6.8	1.5×10^{9}	b

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Table 3. Comparison of Some Rate Constants for Reactions of SO_3^-, SO_5^-, and SO_4^- with Organic Compounds (in $M^{-1}s^{-1}$)

Reactant	SO_3^-	SO_5^-	SO_4^-
ascorbic	$<10^{6}$	2×10^{6a}	*
ascorbate	9×10^{6}	1.4×10^{8a}	*
trolox	$\sim 10^{6}$	1.2×10^{7a}	*
aniline	(reverse)	3×10^{6b}	*
N,N-dimethylaniline	(reverse)	1×10^{7b}	*
tyrosine	$<10^{6}$		$\sim 3 \times 10^{9c}$
tryptophan	8×10^{4}		$\sim 2 \times 10^{9c}$
histidine	NR		$\sim 2.5 \times 10^{9c}$
i-ProH	$<10^{3}$		$\sim 8 \times 10^{7c}$
ethanol		$<10^{3d}$	$\sim 3 \times 10^{7c}$
fumarate	$<10^{5}$		$\sim 2 \times 10^{7c}$
succinate	-	-	7.1×10^{6c}
allyl alcohol	NR		1.5×10^{9c}
glycine	$<10^{3}$		$\sim 9 \times 10^{6c}$
HSO_3^-	-	3×10^{6e}	$\sim 10^{9c}$

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